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Localization of substrate-induced modification in the electronic structure of C_{60} at fullerene-metal interfaces

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Photoemission and electron-energy-loss-spectroscopy studies of C_{60} films deposited on Au(110) demonstrate that only the first layer of molecules, directly in contact with the metal substrate, display significant changes in electronic structure. If the Au(110) surface is precovered with Cs it is found that, at 298 K, the Cs can diffuse readily into a C_{60} thin film, preventing the formation of a localized interface. However, if a Cs precovered Au(110) sample is held at 98 K, subsequent deposition of C_{60} results in the formation of a spatially localized interface with only the closest *two* fullerene layers to the original metal surface modified by charge transfer. [S0163-1829(97)07911-3]

INTRODUCTION

The localization of substrate and/or dopant-induced electronic modification of C_{60} layers is an important question to be addressed if C_{60} is to find a general application as a material for the electronics industry. Already, C_{60} has been used as a material in a number of interesting, and potentially useful, device applications.¹⁻³ It has been suggested that metal-fullerene layered structures may lead to additional materials and/or devices with interesting transport properties, and multilayers of Al and C_{60} have already been grown with this in mind.⁴

Bulk crystalline C_{60} forms a series of charge transfer salts (fullerides), A_xC_{60} , upon intercalation of an alkali metal A . When A is either K, Rb, or Cs, the fullerides may either be insulating/semiconducting when $x=4$ or 6,⁵⁻⁷ or behave as metals when $x=1$ (Refs. 8 and 9) or 3.⁵⁻⁷ When single layers of C_{60} are adsorbed on transition¹⁰ or noble metal¹⁰⁻¹² surfaces they too can be metallic or, in the presence of the appropriate amount of alkali metal coadsorbate,^{12,13} insulating. By varying the dopant concentration of a C_{60} film in a spatially localized manner, it should be possible to produce localized changes in electronic structure within the overall C_{60} "matrix." This could possibly lead to devices fabricated entirely from C_{60} and an appropriate dopant.

The electronic structures of C_{60} layers coadsorbed with Cs have already been characterized by electron-energy-loss spectroscopy¹³ (EELS) and ultraviolet photoemission spectroscopy (UPS).^{13,14} The spectroscopic signatures provided by different fullerene oxidation states enable us to determine the degree of (any) modification of C_{60} layers as a function of their proximity to a C_{60} -metal or C_{60} -dopant interface. Cs was chosen from among the alkali metals to act as an interface/dopant material in this series of experiments. It was thought to be a particularly appropriate dopant because it is

the largest nonradioactive alkali metal, and previous studies had indicated that it has a low diffusion coefficient in solid C_{60} .¹⁵ However, we discovered that bulk diffusion was significant even at room temperature and had to carry out localization experiments involving Cs at 98 K.

EXPERIMENT

UPS and EELS measurements were carried out on samples prepared *in situ* in an ultrahigh vacuum (UHV) system which had a base pressure of 5×10^{-11} mbar. The substrate, a Au(110) single crystal, was cleaned by cycles of Ne^+ ion sputtering followed by annealing to restore surface order. Sample cleanliness was monitored by a Varian Auger electron spectrometer (AES) and by EELS at high resolution. The clean, annealed substrate surfaces displayed a clear 1×2 low-energy electron diffraction (LEED) pattern.

Adsorbate coverage was determined from the ratio of substrate and overlayer Auger peaks, C_{60} coverage was calibrated by measuring the Auger peak ratios of the carbon *KLL* peak at 272 eV to the Au peaks at 69 and 356 eV at a coverage produced by saturating the Au(110) surface with C_{60} at a temperature (≈ 600 K) above that required for desorption of the multilayer. The coverage of the resulting *physical* monolayer of C_{60} (which has an areal density of $1.15 \times 10^{18} \text{ m}^{-2}$) we define as 1 ML.

Cs coverage was calibrated by obtaining a saturated Au(110)- $c(2 \times 2)$ Cs layer (as observed by low-energy electron diffraction) at 450 K and by producing Auger growth curves¹⁶ at 98 K. A physical monolayer—a saturated $c(2 \times 2)$ Cs overlayer (Cs adatom density $4.2 \times 10^{18} \text{ m}^{-2}$)—is taken, for clarity, as 1 ML.¹⁷ Cs coverages for each experiment were then obtained by comparing the Au and Cs Auger peak ratios to the calibration curves, rather than using evaporation time, to eliminate errors brought about by any changes in evaporation rate. This method of coverage cali-

bration gives us an estimated error of $\pm 10\%$ in our measured coverages.

After thorough degassing in UHV, 99% pure C_{60} obtained from Texas Fullerenes was evaporated at around 700 K onto the samples from a tantalum crucible. Substrate temperature was carefully controlled by resistive heating or by cooling with a liquid-nitrogen flow, and monitored by a thermocouple tightly inserted into a hole in the side of the sample. The pressure during C_{60} deposition remained between 2×10^{-10} and 6×10^{-10} mbar. Cs was dosed from a commercial SAES getter source, with chamber pressures of 2×10^{-10} mbar during evaporation cycles. Cs coverages of 1 ML and below were obtained both at 298 and 125 K, while higher coverages were stabilized by maintaining the surface at 125 K during deposition and measurement, in analogy with K deposition on Au(110).¹⁸

Photoemission spectra were obtained using a He lamp and a hemispherical electron analyzer (VG100AX). All spectra presented in this paper were obtained using light from the He I line (21.22 eV), with emission due to the He I satellites subtracted. Fermi-level position was determined from spectra obtained from the clean Au(110) substrate. The spectra were obtained integrated over the acceptance angle of the analyzer ($\approx 5^\circ$) and in normal emission geometry.

Electronic excitations of the surface were measured using a Leybold-Heraeus ELS-22 high-resolution electron-energy-loss spectrometer mounted in the instrumentation chamber. Spectra were acquired in the specular geometry, with incidence and reflection angles of 72° at a primary beam energy of 12 eV, unless otherwise indicated. Because the electronic excitations of a C_{60} -based film have a rather small cross section at low primary beam energies, spectrometer resolution was degraded to between 30 and 50 meV to obtain good signal-to-noise ratio. The intrinsic widths of electronic excitations measured, apart from the fine structure of the low-energy excitons,¹⁹ are significantly greater than this reduced resolution.

RESULTS AND DISCUSSION

When C_{60} is coadsorbed with an alkali metal, even one as large as Cs, interdiffusion may be a significant feature, and could obscure any influence of C_{60} - C_{60} interlayer coupling upon delocalization of any substrate-induced modification. Therefore, for the initial studies of charge-transfer localization we used Au(110), which has a high cohesive energy (and is hence unlikely to diffuse into a C_{60} film) as a substrate. C_{60} forms a chemisorption bond with the Au(110) surface¹⁰⁻¹² resulting in charge transfer to the C_{60} molecules. This change in the oxidation state of the C_{60} molecules leads to a significant change in electronic excitation and photoemission spectra. Therefore, if the electronic structure of the adsorbed C_{60} is followed as a function of coverage it provides a measure of the region to which the charge transfer from the surface is limited.

The results of just such a measurement, using EELS, are shown in Fig. 1. The single monolayer of C_{60} on Au(110) is metallic.^{10,14,20} The higher electronic excitations are broadened and shifted with respect to the bulk and there is no evidence of the band gap and excitonic features seen in pristine, multilayer C_{60} . The spectrum obtained from 2 ML of

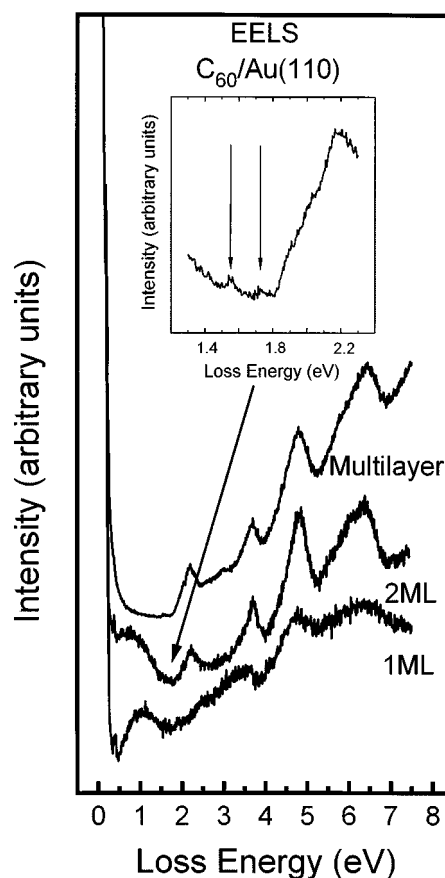


FIG. 1. EEL spectra, obtained in specular geometry with a primary beam energy of 20 eV, of 1 ML, 2 ML, and a multilayer of C_{60} on Au(110). The inset shows exciton losses that are visible in the loss spectrum of the 2 ML film, obtained with better resolution and counting statistics. The presence of excitonic losses in the 2 ML film indicates that it is semiconducting.

C_{60} on Au(110) shows a marked sharpening of the electronic excitations above 2 eV loss energy, which appear at the same energy and have a similar width to the transitions of a multilayer film. Furthermore, a band gap is seen in the second layer spectrum upon which the low-energy electronic excitations of the first monolayer are superimposed. That this really is a band gap is clearly demonstrated by the spectral region shown in the inset of Fig. 1, obtained with higher resolution and better signal-to-noise ratio. Excitonic features are present in the gap at 1.55 eV and above,¹⁹ a clear signature of a semiconducting or insulating layer. Consideration of scanning tunnel microscope measurements²¹ shows that the spectra which we obtain for 1 and 2 ML C_{60} films really correspond to single layer and bilayer films. When C_{60} is grown on Au(110), Au(111), or Ag(111) at room temperature a clear layer-by-layer growth mechanism is observed for at least the first two monolayers.

The presence of strong features associated with pristine C_{60} in the excitation spectrum from the 2 ML film suggests that upon adsorption at the Au(110) surface only the C_{60} layer in direct contact with the substrate is modified, i.e., the second layer is decoupled from the interaction, in agreement with the near-edge x-ray-absorption fine structure results of Maxwell *et al.*¹¹ This interpretation is confirmed by the pho-

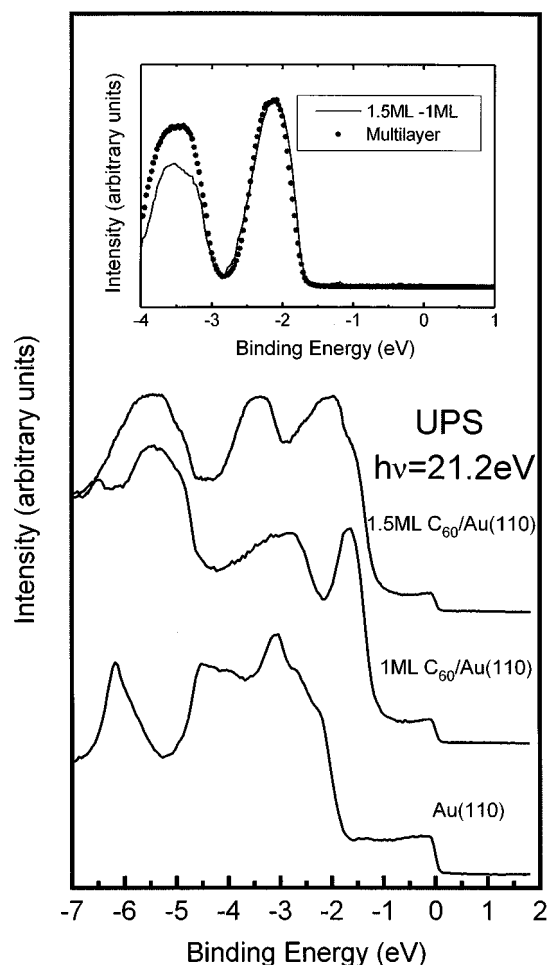


FIG. 2. Photoemission spectra of clean Au(110), 1.0 ML C_{60} , and 1.5 ML C_{60} adsorbed on Au(110). The spectra from the C_{60} covered surfaces are normalized to LUMO peak intensity. The inset shows a comparison between the difference spectrum of the 1.0 and 1.5 ML films and that of a multilayer, shifted 0.5 eV to lower-binding energy. The good agreement between multilayer and difference spectra demonstrates that the second-layer molecules are not strongly perturbed by the substrate.

Photoemission spectra of Fig. 2. The photoemission features of molecules in a second, incomplete, C_{60} layer (total coverage 1.5 ML) show a clear shift to higher-binding energy in comparison to the first, and are significantly sharper, consistent with a localization of substrate-induced changes to the first C_{60} monolayer.

A difference spectrum between the 1 and 1.5 ML films (inset, Fig. 2) was obtained by subtracting the emission of the monolayer film, weighted to the near Fermi-edge region from the 1.5 ML spectrum. A comparison between the difference spectrum and that obtained from a pristine multilayer film shifted 0.5 eV to lower-binding energy is shown in the inset of Fig. 2, the agreement is extremely good. The necessity of shifting the multilayer spectrum to lower-binding energy to obtain a good agreement with the difference spectrum can be explained simply in terms of the screening due to the metallic first monolayer and the substrate. Bulk C_{60} is an insulator and the screening of a photoemission hole is consequently poorer than that of an unperturbed layer in close proximity to a metal. The observed localization of the

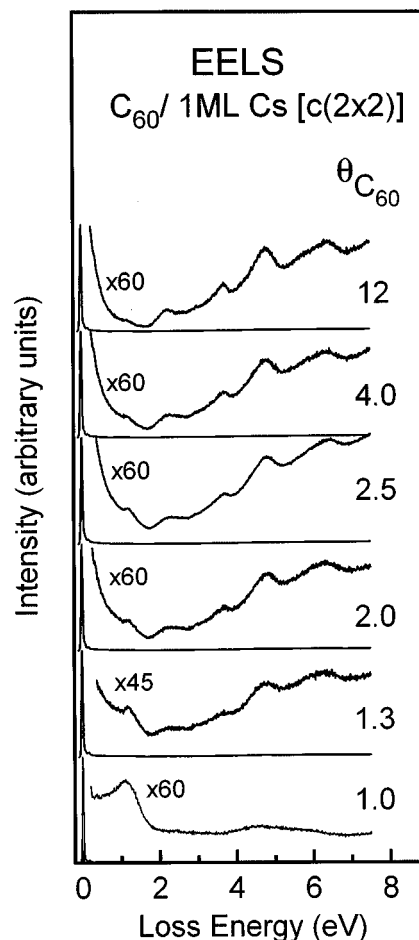


FIG. 3. EEL spectra of C_{60} on an Au(110) surface precovered with a $c(2 \times 2)$ Cs layer, as a function of Cs coverage. Deposition and measurements were made at 298 K. Low-energy loss features persist even to 12 ML of C_{60} , indicating Cs diffusion into the fullerene film. Spectra are obtained in specular geometry at 12 eV beam energy and are normalized to elastic peak intensity.

substrate-induced modification of C_{60} molecules to those molecules in direct contact with the substrate, shows that in the absence of “forced” interdiffusion (e.g., due to an applied electric field^{3,22}) the C_{60} -metal interface is molecularly abrupt.

Localization of charge transfer to C_{60} in the presence of coadsorbed Cs was first explored at room temperature. Cs was chosen as the alkali dopant for this series of experiments because it is the largest of the nonradioactive alkali-metal atoms and was hence the least likely to show diffusion into adjacent C_{60} layers. In fact, in previous experiments the low diffusivity of Cs in C_{60} had led to difficulties in forming homogeneous samples by vapor deposition techniques.¹⁵

Figure 3 shows electronic excitation spectra of C_{60} deposited on a Au(110) surface precovered with 1 ML Cs [a saturated $c(2 \times 2)$ Cs layer] at 298 K. Deposition of C_{60} at this temperature produced films which displayed a strong specular EELS beam, indicative of a relatively high degree of order. The first C_{60} monolayer displays a spectrum of excitations characteristic of C_{60} molecules in an oxidation state of -3 .^{12,13} Subsequent deposition of C_{60} leads to an excitation spectrum rather reminiscent of A_1C_{60} (Refs. 8 and

9) with a strong low-energy background, characteristic of a metal or narrow-gap semiconductor, and a smooth broad peak at about 2.2 eV. In fact, the detailed shape of the 2.2-eV peak and the presence of a small peak at 1.1 eV suggest the coexistence of dimer and ortho-polymer or monomer A_1C_{60} phases.⁸ As coverage increases, the intensity of the low-energy electronic excitations decreases slowly with respect to those at higher-loss energy. However, even at 12 ML C_{60} coverage the low-energy tail to the elastic peak is still present and the higher-lying excitations are still broader than in the pristine material (Fig. 1) suggesting that a significant quantity of Cs resides in the upper layers of this multilayer film.

In the specular geometry, electron-energy-loss spectroscopy from an ordered film can probe more than the outermost layer of C_{60} molecules. This reduction in surface sensitivity arises from a coupling between the long-range electric fields of the incident electron and those from dipole-active excitations below the sample surface.²³ In fact, under the experimental conditions used, the escape depth is calculated to be ≈ 15 Å for a loss energy of 1.0 eV (this value decreases with increasing loss energy). In consequence, around 40% of the low-energy loss intensity originates from the outermost C_{60} layer, which has a thickness of about 8 Å. Therefore, we turn to photoemission measurements, both to obtain a slightly higher degree of surface sensitivity (escape depth 8 Å or less²⁴ for He I radiation) and to provide information about electronic structure complementary to that obtained from EELS.

Photoemission spectra as a function of C_{60} deposition on Au(110)- $c(2 \times 2)$ Cs are shown in Figs. 4 and 5. A single monolayer of C_{60} on the $c(2 \times 2)$ Cs surface shows a broad highest-occupied molecular orbital (HOMO) derived peak and strong Fermi-edge emission, as seen previously.¹³ As coverage is increased, the photoemission peaks at binding energies greater than about 1 eV become progressively narrower and more pronounced, with the HOMO and HOMO-1 derived peaks moving gradually to higher-binding energies. The near Fermi-edge region changes form and appears to consist of a superposition of two distinct components: a broad "hump" intersecting the Fermi level with a high binding energy tail, centered at about 0.3 eV, and a sharper, symmetric, peak centered at about 1 eV binding energy. The general shape of the former feature is characteristic of A_1C_{60} in either the polymer or monomer phase.^{8,9} The presence of the second peak prevents accurate differentiation between the signatures of these two A_1C_{60} phases. The second peak has the same binding energy as, but a different shape to, that observed for a rapidly quenched A_1C_{60} sample containing a large fraction of C_{60} dimers.^{9,25} This difference in peak shape will be considered in detail elsewhere.⁹

The shape and intensity of the near Fermi-edge region changes little between 2 and 4 ML. Beyond 4 ML (corresponding to a global stoichiometry of about $Cs_{0.9}C_{60}$), the near-Fermi-edge emission begins to decrease but remains significant even at a coverage of 12 ML. Using an escape depth of 8 Å for the photoelectrons, the first layer signal should be attenuated by a factor of 10^5 . Even if the interaction with the substrate were extended over three C_{60} layers, the near-Fermi-edge region should be attenuated by a factor of 10^4 . Therefore, the continued presence of a "substrate"

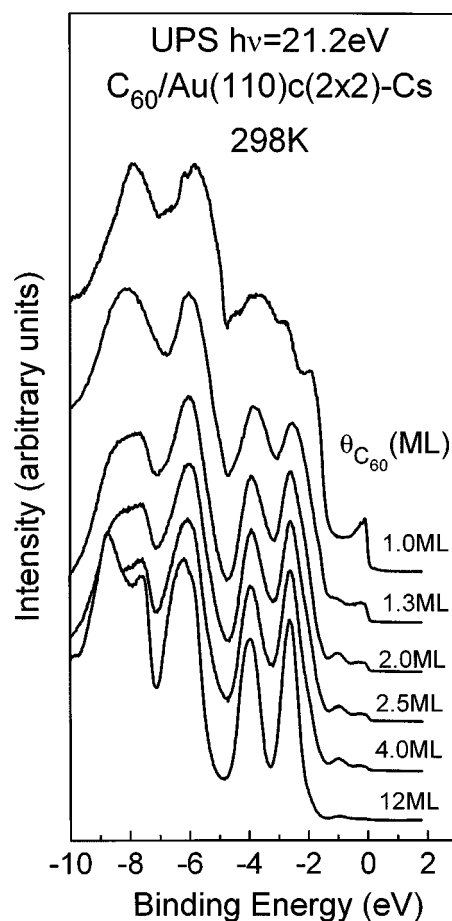


FIG. 4. Photoemission spectra of C_{60} on Au(110) precovered with a $c(2 \times 2)$ Cs layer, as a function of C_{60} coverage. Deposition and measurement were made at 298 K. Spectra are normalized to total photoemission intensity.

induced modification in the surface of a C_{60} film of 12 ML coverage indicates that Cs atoms can diffuse throughout the film at 298 K, and that at this temperature there is no localized C_{60} -alkali-metal interface.

To overcome the problems of interdiffusion, we carried out a similar series of measurements on a sample cooled to 98 K. In order to thoroughly test the efficacy of cooling, a greater Cs precoverage—4 ML as opposed to 1 ML—was used. Although strict layer-by-layer growth of C_{60} is unlikely to occur at low temperature, AES growth-curve measurements indicate that clustering of C_{60} molecules (three-dimensional growth) is not strong for coverages of a few monolayers. The absence of strong three-dimensional growth is further illustrated by the development of the electronic excitation spectra as a function of C_{60} coverage, as shown in Fig. 6. At 0.5 ML C_{60} coverage, we see the features of a -6 C_{60} oxidation state (a band gap of low-loss intensity below ≈ 0.7 eV and a strong peak at 1.34 eV), along with emission in the "gap" region arising from the filling of the LUMO+1 derived states.¹³ Such filling of the LUMO+1 of C_{60} has previously been observed by photoemission in the presence of excess alkali metal.^{25,26} As coverage increases to 1 ML, the features associated with the -6 oxidation state completely dominate the spectrum. If three-dimensional island growth were strong, one would expect to observe the

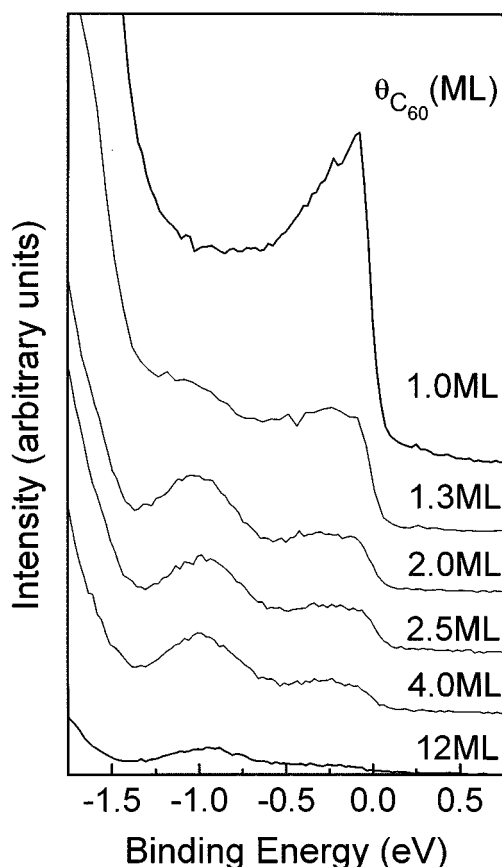


FIG. 5. Near Fermi-edge region of photoemission spectra of C_{60} deposited on an Au(110) $c(2 \times 2)$ Cs surface at 298 K. Spectra are normalized to total photoemission intensity.

“fingerprint” of more than one C_{60} oxidation state at this nominal coverage.

At a coverage of 2 ML C_{60} the strong low-energy loss tail associated with A_1C_{60} (Refs. 8 and 9) once again appears, but rapidly decreases in intensity with subsequent deposition of C_{60} . Indeed, even at 2.5 ML coverage the higher lying excitations begin to sharpen dramatically compared to lower coverages, and approach the width of those in a pristine multilayer. At 3.2(5) ML coverage, the electronic excitation spectrum is almost indistinguishable from a pristine thick film, displaying sharp transitions, a well-pronounced band gap and an excitonic loss at 1.55 eV (see inset, Fig. 6).

It should be noted that the films grown at 98 K are rather disordered, and hence do not produce a specular EELS beam. Under such conditions, electrons which undergo dipole scattering are distributed over a wide angular range, and therefore, even in a nominally specular geometry the intensity of dipole-active losses becomes comparable to those that are excited by impact scattering.²³ The escape depth of the electrons scattered by the impact mechanism is determined by the inelastic mean-free path of the electrons in the C_{60} film rather than the coupling of the electric fields of the incident electrons and near-surface excitations (dipole scattering).²³ At the primary energies that we use to acquire the spectra presented in Fig. 6, the inelastic mean-free path (escape depth) of the electrons has been measured to be 8 Å or less.¹⁹ In consequence, a large (although not directly quantifiable) proportion of the intensity of the spectra shown in Fig. 6

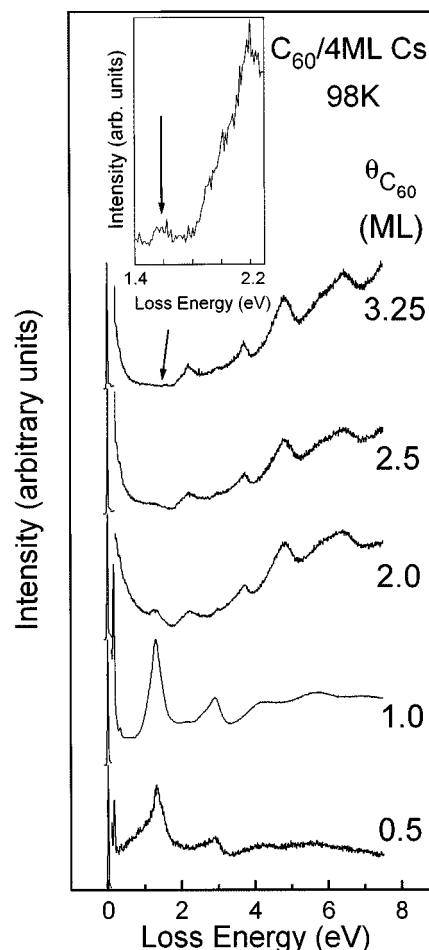


FIG. 6. EEL spectra of C_{60} on an Au(110) surface precovered with 4 ML Cs, as a function of C_{60} coverage. Growth and measurement were carried out at 98 K. Spectra were acquired in specular geometry at a primary energy of 12 eV and are normalized to elastic-peak intensities. The inset shows an expanded region of the 3.25 ML spectrum displaying the excitonic features characteristic of a semiconducting C_{60} layer.

arises from the outermost layer of fullerene molecules. The high degree of surface sensitivity displayed in these EEL spectra explain the lack of any strong features arising from the layers below.

Photoemission (Figs. 7 and 8) tells the same story as EELS. 1 ML of C_{60} on 4 ML Cs displays a spectrum indicating a complete filling of the C_{60} LUMO-derived band, i.e., a fullerene oxidation state of -6 . At 2 ML coverage the photoemission spectrum is similar to that seen at C_{60} coverages between 2 and 4 ML on 1 ML Cs at 298 K. When a coverage of 3.2(5) ML is reached, the spectrum is dominated by emission from pristine C_{60} . The intensity between the HOMO edge and E_F is about 15% of that in the 2 ML C_{60} spectrum, normalizing to HOMO peak heights. This level of intensity is consistent with emission from an unperturbed top layer with an attenuated contribution from the layers below. The degree of attenuation indicates an electron escape depth in these spectra of one C_{60} monolayer (8 Å) or less,²⁴ and therefore supports our conclusion that growth at 98 K is still predominantly layer by layer.

Therefore, at 98 K, a rapid decrease in the intensity of

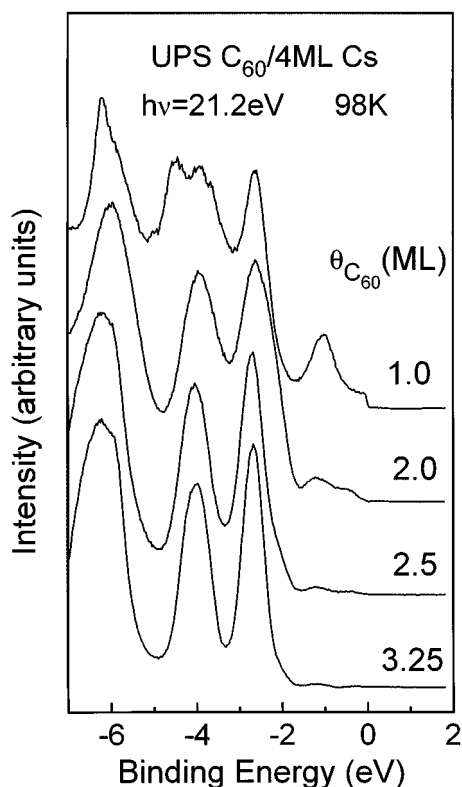


FIG. 7. Photoemission spectra of C_{60} on an Au(110) surface precovered with 4 ML Cs, as a function of coverage. Deposition and measurement were made at 98 K. Spectra are normalized to total photoemission intensity.

features associated with charge-transfer induced modification of C_{60} occurs with increasing C_{60} coverage, indicating that at this temperature the interface between a C_{60} film and a multilayer of Cs is localized. However, a modification of the properties of second layer C_{60} molecules occurs, probably due to the fact that limited interdiffusion is necessary to bring about a -6 oxidation state in the first layer of molecules.¹³ Diffusion of Cs atoms to the vacuum side of a monolayer film leads to direct contact between Cs atoms and second layer C_{60} molecules when a second fullerene layer is grown on the first. The reduced Cs diffusion coefficient at 98 K then prevents further migration of Cs atoms into the C_{60} film, at least over periods of the order of 12 h.

A similar intermixing, limited to the first two C_{60} monolayers, has been observed by Benning and co-workers⁶ when C_{60} was deposited on a 15 Å K film at temperatures below 100 K. It was suggested that charge transfer at the C_{60} -alkali-metal interfaces creates a large-dipole field that drives some alkali atoms to “interstitial” sites on the vacuum side of a first C_{60} layer. Once electrostatic forces have been balanced by a limited diffusion of the alkali atoms, the driving energy for further intercalation is reduced. At 98 K it appears that once the interface dipole has been balanced, Cs [and, for <100 K, K (Ref. 6)] adatoms do not have enough thermal energy to overcome the activation barrier for further diffusion into the C_{60} lattice.

However, when C_{60} films on K multilayers are warmed to around 100 K, Benning *et al.*⁶ have seen intermixing, similar to that observed by Jiang and Koel²⁷ when C_{60} is deposited on a K film held at 100 K. In contrast, we have observed that

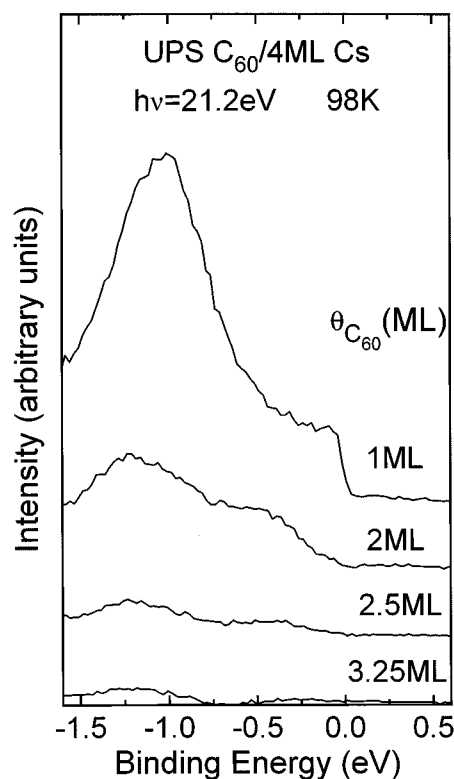


FIG. 8. Near-Fermi-edge region of photoemission spectra of C_{60} on a 4 ML Cs film grown on Au(110), as a function of C_{60} coverage. Data acquisition and C_{60} evaporation were made at a sample temperature of 98 K. Spectra are normalized to total photoemission intensity.

even at 125 K, Cs diffusion beyond the second layer does not occur over a 12 h period. A probable explanation for this difference is that the smaller size of the K ions makes diffusion through the C_{60} matrix easier. Therefore, lower temperatures are required to localize a K- C_{60} interface.

One of the important features in electronic material, in particular one in which superconductivity is desired, is crystalline order. Poor ordering makes the properties of the structures difficult to predict, and will reduce the transition temperature of a superconducting phase. This latter point is illustrated by the differing transition temperatures of bulk K_3C_{60} single crystals and thin films, consisting of 60 Å grains of the same composition, the former superconduct at 18 K,²⁸ the latter at 12 K.²⁹ The two-dimensional lateral disorder inherent in the Cs/ C_{60} interfaces grown at low temperature was reflected in the poor resolution (around 10–12 meV) of vibrational EEL spectra from these surfaces (not shown), an absence of specular electron-energy loss beams, and in the absence of LEED patterns from the surfaces of these structures. Therefore, to produce well-ordered structures which are likely to possess well-defined transport properties we need to investigate the possibility of using dopant materials which remain localized at higher-growth temperatures, which would promote a greater degree of crystalline order.³⁰

CONCLUSIONS

Photoemission and electron-energy loss measurements on C_{60} -metal interfaces as a function of C_{60} coverage have been

carried out. Our results show that modification of the electronic structure of the C_{60} molecules is limited to those molecules *in direct contact* with a substrate or dopant material, i.e., the coupling between C_{60} molecules is rather weak. However, while this modification is highly spatially localized, we find that for Cs at room temperature (298 K) the substrate material (i.e., the Cs film) itself is not and readily diffuses throughout the C_{60} film leading to a nonlocal interface.

Therefore, when using Cs as a dopant, it is necessary to maintain any interface at low temperature (≈ 98 K) in order to prevent large-scale diffusion of Cs into the “undoped” regions of the interface. The requirement for low temperature

means that crystallinity is lost for the sake of localization, producing a likely reduction in the quality of the electronic transport properties of the resulting interface. Hence, in order to produce C_{60} based materials, with localized differences in electronic structure, it is necessary also to explore the possibility of using other dopant materials which will remain localized under conditions (particularly elevated temperature) under which ordered films can be grown.³⁰

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